

Preparation of the porous cerium dioxide film by two-step anodization and heat treating method

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Abstract. The porous cerium dioxide films were prepared with cerium foils as raw materials by two-step anodization and heat treating method. The anodic cerium oxide films were heat treated in 25~400°C respectively. The cerium dioxide films were characterized with X-ray diffraction (XRD), Fourier transform infrared (FTIR) techniques, energy-dispersive analyses of X-ray (EDAX) and scanning electron microcopy (SEM), respectively. The anodic cerium oxide film is composed of Ce(OH)₃, CeO₂ and Ce₂O₃. When the anodic cerium oxide films were heat treated in 300°C~400°C for 2h, Ce(OH)₃ and Ce₂O₃ in the anodic cerium oxide films may be converted to CeO₂, and the heat treated anodic cerium oxide films are the cerium dioxide films. Water, ethylene glycol and CO₂ are adsorbed in the anodic cerium oxide film. The adsorbing water, ethylene glycol and CO₂ in the anodic cerium oxide film are removed at 300°C. The cerium dioxide film has strong absorption in the range of 1600~4000cm⁻¹. The structure of the cerium dioxide film is the porous.

1. Introduction

Cerium dioxide has recently been attracting much attention in the oxidative catalysis and solid oxide fuel cell (SOFC) research communities due to its high oxygen storage capacity and replacement of yttrium stabilized zirconia as the electrolyte for great reduction operating temperature [1-6]. The porous film structures are potentially suitable for efficient catalytic treatment of reactants because such structures do not aggregate like particles, and the aggregation of particles have diminished effective catalytic surface areas when used in bulk forms. The porous films can also serve as products on different sides of the films such as in SOFC and media for separating reactants. The common preparation methods of the porous cerium dioxide films are as follows. The CeO₂ powders and pore-forming agents were mixed with distilled water and dispersants and ball-milled to obtain a homogeneous suspension. After ball-milling, the binders and plasticizers were mechanically mixed with the homogeneous suspension to obtain a suspension. Then, the mixture films were prepared with the suspension. The mixture films were sintered at 1450 °C, and the porous cerium dioxide films were



got. But there are some problems, such as the increase of CeO_2 particle sizes and decrease of the effective surface area of the film by high sintering temperature, controllability of thickness of the film, the holes of the films being tortuous holes and high cost. If the porous cerium dioxide films will be prepared with cerium foils as raw materials by two-step anodization, we may solve the above problems.

In this paper, the porous cerium dioxide films were prepared with cerium foils as raw materials by two-step anodization and heat treating method. The anodic cerium oxide films were heat treated in $25^\circ\text{C}\sim 400^\circ\text{C}$ respectively. The cerium dioxide films were characterized with X-ray diffraction (XRD), Fourier transform infrared (FTIR) techniques, energy-dispersive analyses of X-ray (EDAX) and scanning electron microcopy (SEM), respectively.

2. Experimental

2.1. Preparation of the cerium dioxide films

The cerium dioxide films were prepared by two-step anodization and heat treating method according to [7]. High purity cerium foils (99.99% purity, $15\text{mm}\times 15\text{mm}\times 0.3\text{mm}$) were used to grow anodic porous layers. The cerium foils were degreased in absolute ethyl alcohol by using ultrasonic cleaner and annealed at 500°C for 3h to remove mechanical stresses and recrystallization of the cerium foils under a nitrogen atmosphere, and then polished with diamond spray polishing agent, washed in absolute ethyl alcohol by using ultrasonic cleaner before anodization. An electrochemical reactor was designed and built to carry out anodizing experiments. After anodizing for 2h, the anodized specimen was immersed in 35% HNO_3 -2% H_2O_2 solution at 70°C for 10 minutes to remove the oxide layer on the anodized specimen, dried with an air jet, anodized. The electrolytes were $1\text{mol/LNH}_3\cdot\text{H}_2\text{O}$ aqueous ethylene glycol solution, ethylene glycol : $\text{H}_2\text{O} = 10 : 1$. The anodizing parameters: temperature 20°C , current density $1\text{mA}/\text{cm}^2$, time 10 h. After anodizing, the anodized specimen was washed thoroughly with distilled water, dried with an air jet, the anodized specimen was heat treated for 2 h, and the cerium dioxide film was got.

2.2. Testing instruments and methods

X-ray powder diffraction patterns of the anodic cerium oxide film and heat treated anodic cerium oxide films were acquired with a Rigaku D/max 2550 VB/PC X-ray diffractometer, using $\text{Cu K}\alpha$ radiation, respectively. A continuous scan mode was used to collect 2θ data from $10\sim 70^\circ$ with a 0.02 sampling pitch and a 2°min^{-1} scan rate. X-ray tube voltage and current were set at 40 kV and 30 mA, respectively.

Infrared absorption spectra of the anodic cerium oxide film and the heat treated anodic cerium oxide film of heat treatment at 300°C for 2h were determined by Avatar 360 FTIR infrared spectrophotometer by potassium bromide disc method respectively.

The energy-dispersive analysis of X-ray of the heat treated anodic cerium oxide film of heat treatment at 300°C for 2h was acquired with S-3400N scanning electron microcopy.

The morphology of the cerium dioxide films were examined by HITACHI S3400 scanning electron microcopy.

3. Results and discussion

3.1. XRD studies

The X-ray diffraction patterns of the anodic cerium oxide films at different heat treating temperature are shown in Fig.1. As shown in Fig.1a, the anodic cerium oxide film has the diffraction patterns at 16.105° , 28.776° , 30.093° , 32.069° , 33.346° , 40.150° , 40.301° , 42.401° , 47.693° , 48.402° , 49.289° , 56.572° , 59.386° , 62.678° , 69.982° , respectively, the diffraction peaks correspond to hexagonal $\text{Ce}(\text{OH})_3(100)$, cubic $\text{CeO}_2(111)$, hexagonal $\text{Ce}_2\text{O}_3(011)$, $\text{Ce}(\text{OH})_3(200)$, cubic $\text{CeO}_2(200)$, hexagonal $\text{Ce}_2\text{O}_3(102)$, $\text{Ce}(\text{OH})_3(201)$, $\text{Ce}(\text{OH})_3(210)$, cubic $\text{CeO}_2(220)$, hexagonal $\text{Ce}(\text{OH})_3(300)$, $\text{Ce}(\text{OH})_3(211)$,

cubic $\text{CeO}_2(311)$, $\text{CeO}_2(222)$, hexagonal $\text{Ce}_2\text{O}_3(202)$, cubic $\text{CeO}_2(400)$, respectively. The anodic cerium oxide film is composed of $\text{Ce}(\text{OH})_3$, CeO_2 and Ce_2O_3 . Comparing Fig.1b, Fig.1c to Fig.1a, when the anodic cerium oxide films were heat treated in $300^\circ\text{C}\sim 400^\circ\text{C}$ for 2h, the heat treated anodic cerium oxide films have not the diffraction patterns at 16.105° , 30.093° , 32.069° , 40.150° , 40.301° , 42.401° , 48.402° , 49.289° , 62.678° , respectively, demonstrating the transformation of $\text{Ce}(\text{OH})_3$ and Ce_2O_3 in the anodic cerium oxide films into CeO_2 . The heat treated anodic cerium oxide films are the cerium dioxide films.

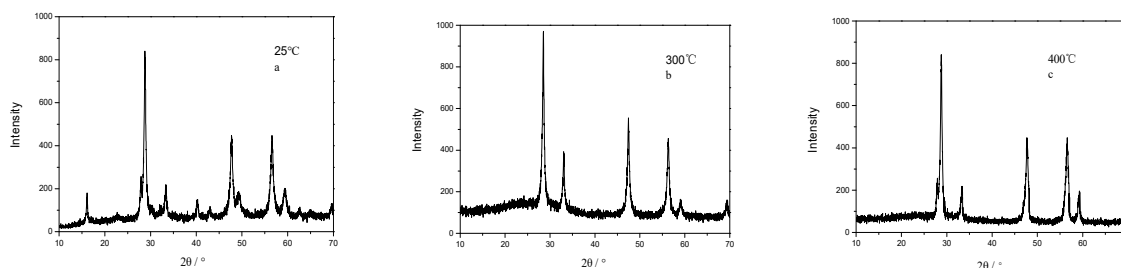


Fig.1 XRD spectra of the anodic cerium oxide films at different heat treating temperature

3.2. Infrared spectra

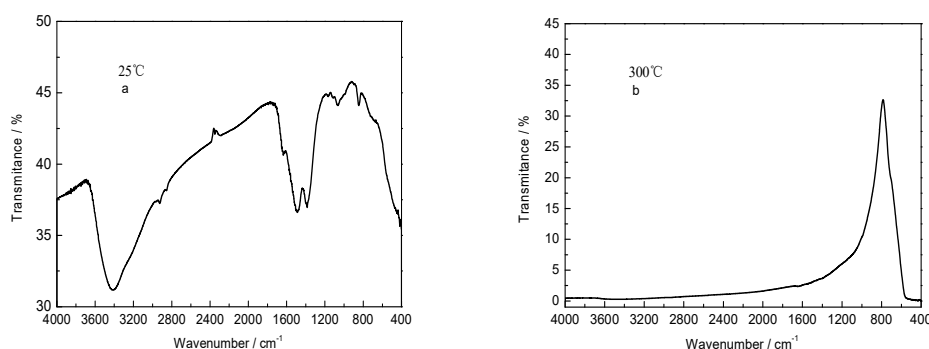


Fig.2 FTIR spectra of the anodic cerium oxide film and the heat treated anodic cerium oxide film

FTIR spectra of the anodic cerium oxide film and the heat treated anodic cerium oxide film of heat treatment at 300°C for 2h are shown in Fig.2. According to Fig.2a, there are $\nu\text{O-H}$ vibration peak at 3418.35cm^{-1} , νCO_2 vibration peak at 2349.45cm^{-1} , $\nu\text{O-H}$ vibration peak at 1644.57cm^{-1} , δCH_2 vibration peak at 1538.02cm^{-1} , $\delta\text{O-H}$ vibration peak at 1384.70cm^{-1} , $\nu\text{C-O}$ vibration peak at 1064.08cm^{-1} , CeO_2 vibration peak at 400cm^{-1} ^[8], demonstrating the presence of adsorbing water, ethylene glycol and CO_2 in the anodic cerium oxide film. According to Fig.2b, there is CeO_2 vibration peak at 435.85cm^{-1} , demonstrating the heat treated anodic cerium oxide film of heat treatment at 300°C for 2h being cerium dioxide film. The adsorbing water, ethylene glycol and CO_2 in the anodic cerium oxide film are removed at 300°C . The result is consistent with the XRD analyses result. The cerium dioxide film has strong absorption in the range of $1600\sim 4000\text{cm}^{-1}$.

3.3. EDAX analysis

The EDAX spectrum of the heat treated anodic cerium oxide film of heat treatment at 300°C for 2h is shown in Fig.3. The contents of $\text{Ce}(\text{at}\%)$ and $\text{O}(\text{at}\%)$ are 32.32% and 67.68% respectively, and $\text{Ce}(\text{at}\%) : \text{O}(\text{at}\%) = 1 : 2$. The heat treated anodic cerium oxide film of heat treatment at 300°C for 2h is cerium dioxide film. The results are consistent with the XRD and FTIR analyses results respectively.

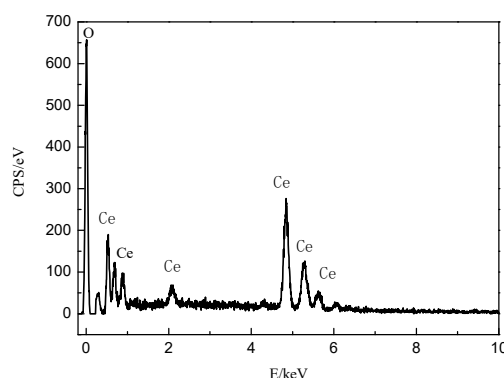
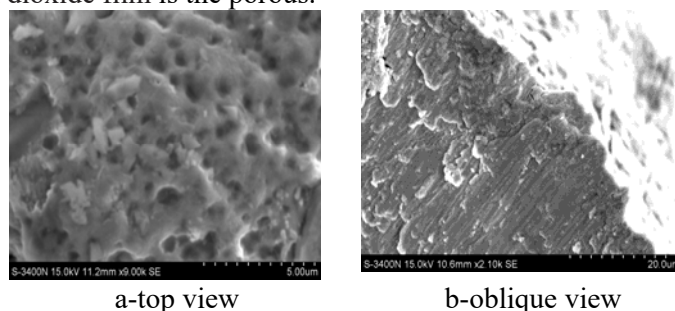


Fig.3 EDAX spectrum of the heat treated anodic cerium oxide film of heat treatment at 300°C for 2h

3.4. SEM image

SEM surface morphologies of the cerium dioxide film are shown in Fig.4. It is seen in Fig.4 that, the structure of the cerium dioxide film is the porous.



a-top view

b-oblique view

Fig.4 SEM of the cerium dioxide film

4. Conclusions

The porous cerium dioxide films are prepared with cerium foils as raw materials by two-step anodization and heat treating method. The anodic cerium oxide film is composed of $\text{Ce}(\text{OH})_3$, CeO_2 and Ce_2O_3 . When the anodic cerium oxide films were heat treated in 300°C~400°C for 2h, $\text{Ce}(\text{OH})_3$ and Ce_2O_3 in the anodic cerium oxide films may be converted to CeO_2 , and the heat treated anodic cerium oxide films are the cerium dioxide films. Water, ethylene glycol and CO_2 are adsorbed in the anodic cerium oxide film. The adsorbing water, ethylene glycol and CO_2 in the anodic cerium oxide film are removed at 300°C. The cerium dioxide film has strong absorption in the range of 1600~4000 cm^{-1} . The structure of the cerium dioxide film is the porous.

Acknowledgements

This work was financially supported by the project supported by the National Natural Science Foundation of China (51372153, 51572176), Shanghai Municipal Education Commission (Plateau Discipline Construction Program, 0817), Collaborative Innovation Fund of Shanghai Institute of Technology (XTCX2017-5).

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